TITLE: COLLECTIVE RELAXATION, SINGLE PARTICLE MOTION AND SHORT RANGE ORDER IN α'-NBD$_X$: A QUASIELASTIC NEUTRON SCATTERING STUDY

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COLLECTIVE RELAXATION, SINGLE PARTICLE MOTION AND SHORT RANGE ORDER IN α'-NbD$_x$: A QUASIELASTIC NEUTRON SCATTERING STUDY

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Summary

Applying both incoherent and coherent quasielastic neutron scattering we have studied simultaneously single particle motion, collective relaxation and short range order of deuterium in α'-NbD$_x$. A comparison with recent Monte Carlo simulations lead to a consistent description of all results in terms of strongly repulsive deuterium-deuterium interactions. Relating the independently determined tracer and chemical diffusion coefficients with the also measured structure factor we show experimentally that for lattice gases the de Gennes narrowing Ansatz needs to be modified by correlation factors.

Introduction

Studying the diffusive behavior of an ensemble of particles we may probe for two essentially different modes of relaxation: (i) the single particle motion which in the long time limit leads to the tracer diffusion coefficient D_t and (ii) the collective relaxation of density fluctuations asymptotically related to the Fick—or chemical—diffusion coefficient D_{chem}. Both phenomena are different aspects of the underlying microscopic motions governed by single particle jump mechanisms and interparticle interactions. Applying quasielastic neutron scattering as a microscopic probe the first is measured in an incoherent scattering experiment probing the self correlation function while the latter is revealed from coherent scattering sensitive to pair correlations[1].

In this brief communication[2] we present the first dynamic study where both quantities have been investigated simultaneously in one experiment. We exploited the similarity of the coherent and incoherent neutron cross sections of deuterium ($\sigma_{coh} = 5.6b$, $\sigma_{inc} = 2.0b$) and chose the lattice gas system NbD$_x$. At high deuterium concentration pair and self correlations

relax at distinctly different time scales and consequently their separation becomes possible without neutron polarization analysis. Applying a lattice gas model with multiple site blocking[3] we are able to describe single particle and collective dynamics consistently and to relate static and dynamic scattering data. Thereby we show experimentally that for a lattice gas the usual de Gennes narrowing assumption[4, 5] has to be modified with respect to particle correlation factors.

Theory

The quasielastic part of the double differential neutron scattering cross section for scattering from deuterium atoms in NbD_x is given by the sum of an incoherent and coherent contribution:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} = N_D \frac{k_i}{k_f} e^{-2W_D} \left\{ \frac{\sigma_{inc}}{4\pi} \Lambda_{inc} + \frac{\sigma_{coh}}{4\pi} (1-A) S(Q) \Lambda_{coh} \right\} \quad . \tag{1}$$

Thereby N_D is the number of D-atoms in the beam, k_i and k_f are the incident and final wave vectors, and $2W_D$ is the Debye Waller factor which can be calculated using the Debye temperature and the D localized mode frequencies. At small enough momentum transfers $Q (Q \leq 1 \text{ Å}^{-1})$ the incoherent and coherent quasielastic contributions Λ_{inc} and Λ_{coh} are single Lorentzians[1]. Their widths Γ_{inc} and Γ_{coh} are related to the tracer and collective diffusion coefficients by

$$\Gamma_{inc}(Q) = Q^2 D_t \tag{2}$$

and

$$\Gamma_{coh}(Q) = Q^2 D_c(Q) \quad . \tag{3}$$

While the intensity of the incoherent contributions is independent of Q, the coherent intensity follows the coherent structure factor of the deuterium atoms S(Q), provided it is corrected for diffuse scattering originating primarily from Nb-D correlations. In the Q-range of interest this correction A in Eq. 1 does not depend on Q. It is calculated from the elastic data of NbD[6] and amounts to 21% of the coherent intensity[2].

The tracer, or self-diffusion coefficient for a lattice gas, is given by[3]

$$D_t(c) = V(c) \, f_t(c) \, D_0 \qquad (4)$$

where c is the deuterium concentration. V is the so called site availability factor accounting for site blocking due to the presence of a finite deuterium concentration. For tetrahedral sites in a bcc metal (6 per host atom) and single site blocking we have $V(c) = 1 - c/6$; but a more complex expression evolves for multiple site blocking. f_t is the tracer correlation factor describing the reduction of tracer diffusion at finite deuterium concentrations due to the enhanced probability for backward jumps and

$$D_0 = \ell^2 / 6\tau_0 \qquad (5)$$

is the single particle or intrinsic diffusion coefficient in the empty lattice.

The line width of the coherent quasielastic line, Eq. 3, may be regarded as the characteristic time for the formation and disintegration of density fluctuations of the size $2\pi/Q$. For $Q \to 0$ macroscopic density fluctuations are considered and the collective diffusion coefficient $D_c(Q \to o)$ becomes the macroscopic chemical (Fick) diffusion coefficient. Its concentration dependence is given by[3]

$$D_{chem}(c) = V(c) \, f_m(c) \, \gamma_{th}(c) \, D_0 \quad . \qquad (6)$$

The mobility correlation factor f_m accounts for the reduction of D_{chem} due to local rearrangement jumps. For simple site blocking $f_m = 1$, while multiple site blocking mechanisms lead to $f_m < 1$. Note that f_m is always larger than f_t. The thermodynamic factor γ_{th} relates to the driving force, the second derivative of the Gibbs free enthalpy with respect to concentration. For a system executing only concentration-concentration fluctuations like a lattice gas it is the inverse of the structure factor at zero-momentum-transfer:

$$\gamma_{th} = 1/S(0) \quad . \qquad (7)$$

For non-vanishing momentum transfers de Gennes realized that a minimum in $D_c(Q)$ coincides with a maximum in $S(Q)$[4]. This so-called de Gennes narrowing pictorially means that spatially preferred configurations (large $S(Q)$) temporarily disintegrate more slowly. From

the second moment relationship of the scattering function, Sköld derived his well-known *ad-hoc* approximation[5]

$$S_{coh}(Q,\omega) = S_{inc}(Q \cdot S(Q)^{-1/2}, \omega) \cdot S(Q) \quad , \tag{8}$$

which for the line widths at small Q leads to

$$\Gamma_{coh} = \Gamma_{inc} / S(Q) \quad , \tag{9}$$

an equation widely used in the interpretation of quasielastic coherent neutron[7] and light scattering data[8]. We note, however, that it differs from what is expected from correlated motion in a lattice gas where according to Eqs. 2, 3, 4, 6, 7 we have

$$\Gamma_{coh} = \Gamma_{inc} / \{S(Q) \cdot f_t / f_m\} \quad . \tag{10}$$

Finally, we turn to the coherent structure factor $S(Q)$ reflecting the short-range order in the system. The spatially averaged structure factor per D atom can be expressed in terms of the so-called Cowley short-range order parameters α_i[9]

$$S(Q) = [1 - c/6] \sum Z_i \, \alpha_i \sin (Qr_i) / (Qr_i) \tag{11}$$

where r_i is the distance to the "i"-th coordination shell and Z_i the coordination number. For a lattice gas the α_i describe deviations from a random mixture of interstitial vacancies and D-atoms. Negative α_i show that in a coordination shell "i" vacancies are over-represented. Positive α_i are indicative for a higher than average deuterium population in this shell.

Experiment

The neutron scattering experiments were performed at the IN5 multichopper time-of-flight spectrometer of the Institut Laue-Langevin in Grenoble. We investigated cylindrical polycrystalline NbD_x samples with $x = 0.51, 0.63, 0.72$ and 0.85. The measurements were taken in the disordered α'-phase at 418, 486, and 581 K recording 14 spectra simultaneously at Q-values between 0.105 and 1.85 Å^{-1}. The incident wavelength of $\lambda = 6$Å resulted in an energy resolution of about 30 μeV (HWHM). The data were corrected for background and by means of a vanadium calibration run transformed to absolute intensities.

Results

A typical low Q spectrum is displayed in Fig. 1. It was fitted with 1 or 2 Lorentzian lines. The resulting residuals at the top of this figure clearly show the presence of two quasielastic contributions in the spectrum. As a consequence of the different magnitudes of tracer and collective diffusion coefficients, the narrow Lorentzian can be identified due to incoherent scattering; the broad one results from coherent scattering.

The data evaluation in terms of Eq. 1 proceeded in several steps: In pilot fits it was realized that the short range order parameters α_1 and α_2 approached values corresponding to complete blocking. Therefore, in the further evaluation they are kept fixed at these values and we only varied α_3. Higher α_i were kept at zero, because with respect to the accuracy of our data correlations in the fourth and further coordination shells appeared not to be significant. For the determination of D_t, D_c and α_3 Eq. 1 was convoluted with the resolution function of each detector and then simultaneously fitted to eight spectra with $0.23 \, \text{Å}^{-1} \leq Q \leq 1.35 \, \text{Å}^{-1}$, additionally allowing for a common Q and ω independent background. In these fits, we describe the Q dependence of the collective diffusion coefficient by

$$D_c(Q) = \text{const.} / S(Q) \tag{12}$$

in order to be able to experimentally decide between Eq. 9 and Eq. 10. In order to check the validity of the assumed Q dependence, single spectra fits were also performed revealing Q-dependent results for $D_c(Q)$. Multiple scattering corrections were carried out in all fits using the Monte Carlo program DISCUS[10] in a procedure analogous to that described in Ref. 11. Figure 2 presents the Q-dependence of the resulting diffusion coefficients, Fig. 3 displays their concentration and temperature dependencies in comparison with literature data. Table 1 lists the resulting quantities.

Discussion

Commencing with the *short range order parameters*, we now consider the different results in more detail: We found that one deuterium atom completely blocks its four adjacent and the two next neighboring sites for occupation by other deuteriums. Thus, the deuterium-deuterium interactions are strongly repulsive. This repulsion, which is also evident from the increase of the thermodynamic factor with increasing concentration, is most pronounced at the lowest D-concentration of $c = 0.51$, where we observe a significant blocking even of the third

coordination shell (negative α_3). For three shell blocking the maximum deuterium content is limited to $c = 0.8$. Therefore, it is clear that partial blocking of the third shell cannot be realized in concentrated NbD_x: on the contrary, the occupancy of the third shell may become higher than average (positive α_3) in order to accommodate all D-atoms in the interstitial lattice. Our experimental results for α_3 also show that with increasing temperature, short range order effects in the third shell become less important. These effects are also directly visible in the diffusion data of Fig. 3. There, the experimentally observed concentration dependence of the *tracer diffusion coefficient* at 418 K is compared with Monte Carlo results[3] for two and three shell blocking. The data tend to shift from three shell blocking at lower concentration to two shell blocking at higher concentration, a phenomenon which is most pronounced at the lowest temperature. This observation agrees also with conclusions drawn from thermodynamic data like heat capacity measurements[12] · A comparison of those data with Monte Carlo simulations also suggest a scenario between two and three shell blocking[13].

As can be seen from Fig. 2, qualitatively the *collective diffusion coefficients* $D_c(Q)$ exhibit a de Gennes narrowing: they increase inversely to the increase of the structure factor $S(Q)$. Quantitatively, however, for all deuterium concentrations and temperatures, systematic deviations are observed: the D_c values obtained from a simultaneous fit of Eq. 12 (upper solid line in Fig. 2) as well as the D_c values obtained from single spectra fits (black dots in Fig. 2) are larger than those calculated by means of Sköld's *ad-hoc* approximation (Eq. 9) from the D_t values, which were independently determined from the incoherent scattering. The missing factor is easily identified (see Eq. 10) as the ratio f_t / f_m, also called Haven's ratio. Although the resulting value for f_t / f_m (last column in Table 1) are subject to numerical uncertainties, their magnitudes lie within the range of Monte Carlo results for two and three shell blocking[3] (two shell blocking: $f_t / f_m = 0.89$ and 0.72 for $c = 0.51$ and 0.72, respectively; three shell blocking: $f_t / f_m = 0.69$ and 0.60 for $c = 0.51$ and 0.72, respectively). Their increase with temperature again relates to the shift from three to two shell blocking observed in the short range order parameters and the tracer diffusion coefficients. These results also resolve discrepancies found in earlier experiments when results from different techniques, like Gorsky effect and quasielastic neutron scattering, were compared. Potzel et al[14] reported a Haven's ratio of 1.2, which is clearly unphysical and must originate from systematic errors arising when comparing the outcome from different techniques. Such systematic errors may also explain why our values for D_{chem} are systematically higher than earlier Gorsky effects[15] (Fig. 3).

Finally, we remark on the discrepancy between the widely used Sköld approximation of the de Gennes narrowing (Eq. 9) and the lattice gas result (Eq. 10) favored by our data. *Physically*, the Sköld approximation means an effective mass approximation: the collective motion of interacting atoms of mass m is described by the single-particle motion of a cluster of atoms of mass $m \cdot S(Q)$, $S(Q)$ being a measure of the effective number of particles, which contribute at the momentum transfer $\hbar Q$. This is a simple minded way to describe a collective motion; it is incorrect with respect to the fourth, sixth, eighth, etc., moments of the scattering function. A whole series of further developments of this kind of theory have carefully been tested by comparing the respective coherent scattering functions with the neutron scattering data on liquid argon and none of them "gives a completely adequate representation of the data"[17]. Since these much more complex theories did not work out better than Sköld's simple *ad-hoc* approximation, the latter survived. Collective motion is affected by interactions, and this influence can be expressed in terms of correlation factors. Therefore, the second simplest approach—as such we consider ours—must somehow contain these correlation factors. *Formally*, the discrepancy between Eq. 9 and Eq. 10 is due to line-shape effects: excess intensity in the wings of the small Q incoherent neutron scattering function for diffusion in concentrated lattice gases increases the second moment, but does not contribute to the line width at half maximum. Such deviations from a Lorentzian line shape in the intervening region $0 \ll c \ll 1$ have been predicted on the basis of theoretical considerations by Ross and Wilson[13].

Conclusion

In summary, exploiting the coherent and incoherent scattering from deuterium, we have performed a comprehensive quasielastic neutron scattering study on a lattice gas with pronounced repulsive interactions. Based on a hard sphere model involving blocking of the first two neighbor shells and variable occupation of the third shell, we were able to establish a consistent interpretation of the static and dynamic properties in relating the short range order of the deuterium atoms to their single particle and collective motional behavior. For lattice gases the often used empirical Ansatz for the de Gennes narrowing in coherent quasielastic neutron scattering can considerably be improved by introducing the ratio of the correlation factors, in accordance to lattice gas theory. We have demonstrated this experimentally for a metal / deuterium system, but we are convinced that it is equally important for superionic conductors.

Acknowledgement

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Figure Captions

Fig. 1: Quasielastic neutron scattering data for $NbD_{0.85}$ at $Q = 0.80$ and $T = 581$ K: left hand side: fit with one Lorentzian; right hand side: fit with a narrow (incoherent) and a broad (coherent, dashed) Lorentzian; upper part: the respective resulting (statistically weighted) residuals.

Fig. 2: Q dependence of the deuterium diffusion coefficients in $NbD_{0.85}$ at 581 K (left ordinate); the black dots result from a simultaneous fit of Eq. 1 to the data but with $D_c(Q)$ free to vary individually for each Q-value; the upper solid line is the result of a simultaneous fit with the Q dependence of $D_c(Q)$ as in Eq. 12. The lower solid line represents the de Gennes narrowing result $D_c(Q) = D_t / S(Q)$. The black triangles display the coherent deuterium intensities (right ordinate). The dashed line results from the simultaneous fit.

Fig. 3: Resulting dueterium tracer (larger guide dashes) and chemical (solid guide lines) diffusion coefficients in NbD_x (full symbols) in comparison to experimental and theoretical literature data: crosses: well established D_0 values[16], open symbols: chemical diffusion coefficients from [15], upper (lower) small dashes: Monte Carlo results of the tracer diffusion coefficients at 418 K for a two-shell (three-shell) blocking model[3].

Table Caption

Table 1 Tracer diffusion and chemical diffusion coefficients, short range order parameters, thermodynamic factors and Haven's ratio for deuterium diffusion in Nb.